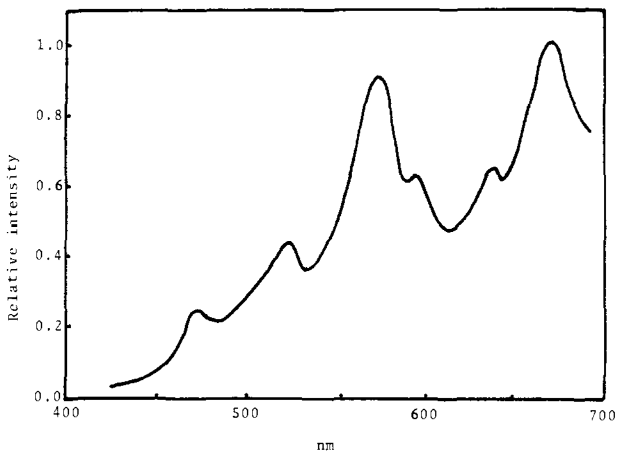

Figure 1. Emission spectrum observed in the reaction of linoleic acid hydroperoxide with ceric ion.

in the reaction of linoleic acid hydroperoxide with ceric ion is shown in Figure 1. The peaks of light emission in the microsomal lipid peroxidation system (between 400 and 680 nm), which have been reported previously, are also presented in the same table (system 3). In the present systems, five characteristic peaks around 470-480, 510-530, 560-580, 630-640, and 670 nm are distinguishable (i.e., quite similar to those of the emission in the microsomal lipid peroxidation system), although the relative intensities of the peaks vary in the different runs. The latter effect is probably caused by the inconstency of the light source. The relative light intensities listed in Table I resemble those from the emission in the reaction of alkali metals in hexamethylphosphoramide with H_2O and O_2 (a heterogeneous system),[10] but differ from those obtained from aqueous H_2O_2-OCl^- systems (a homogeneous system).[12] As five peaks are typical for all the spectra taken with aqueous systems and independent of the *sec*-hydroperoxides, it seems reasonable to assign the emission to transition of $(^1\Sigma_g{}^+)(^1\Delta_g)$ and $(^1\Delta_g)(^1\Delta_g)$ dimers, with the exception of the species peaking near 670 nm.[13] The emitter would not be the excited carbonyl compounds which could be generated in the decomposition of the cyclic intermediate (eq 2).[14] Only one prominent peak around 465-500 nm corresponding to $^1\Sigma_g{}^+ + {}^1\Delta_g \rightarrow 2(^3\Sigma_g{}^-)$, in contrast, was observed during ceric oxidation of *sec*-butyl hydroperoxide in benzene. This discrepancy may be attributable to a different lifetime of the $^1\Sigma_g{}^+$ state in the solvent used. It is well documented that this species is sensitive to water quenching,[3] a result which is consistent with the findings reported here.

We observed D_2O effects on light emission from the aqueous systems.[15] One-tenth milliliter of 7.5×10^{-3} M linoleic acid hydroperoxide (or *sec*-butyl hydroperoxide) in 0.1 M NH_4OH-NH_4Cl buffer (pH 9.0) was mixed with 2.8 ml of D_2O or H_2O and the reaction was initiated by a rapid addition of 0.1 ml of 7.5×10^{-3} M ceric ammonium nitrate. Total light output in the visible region was then determined for the initial 15 min with a photon counter.[16] Under these conditions, the total light output (initial 15 min) of the D_2O system increased 1.5-3.0-fold over that of H_2O system.

In mammalian cells, the membrane and microsome are abundantly rich in unsaturated fatty acids, including linoleic acid. It is expected that $^1O_2$ would be generated by self-reactions of *sec*-peroxy radicals of unsaturated fatty acids produced in the process of peroxidative cleavage of phospholipids, and this expectation is strongly supported by the observed chemiluminescence of the NADPH-dependent microsomal lipoxygenation system[1,2] and microbicidal system of polynuclear leucocytes.[17]

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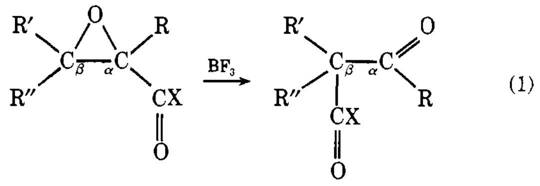
Rearrangement of Optically Active Ethyl (*E*)-3-Methyl-3-phenylglycidate. Evidence for Concerted Carbethoxy Migration

Sir:

The mechanism of the acid-catalyzed rearrangement of acyl groups to adjacent positive centers still remains a subject of controversy.[1] The 1,2-migration of the carbonyl group in α,β-epoxy carbonyl compounds has received particular attention in both mechanistic[1] and synthetic[1b,2] studies (1). Carbonyl migration, catalyzed by boron trifluoride, has been observed with epoxy ketones,[3] esters,[4] and thiol esters.[5] The reaction has been established to be intramolecular by "crossed product" studies.[6] House has also

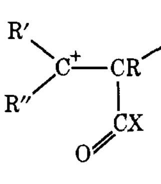


(1)

X = alkyl, aryl, OR, SAr

convincingly demonstrated that in the rearrangement of α,β-epoxy ketones acyl migration is preferred over a hydrogen or primary alkyl shift.[3b,7] Similarly, Kagan has shown that the migratory preference in glycidic esters follows the order phenyl > carbethoxy > methyl.[4]

The 1,2-rearrangement of an electronegative alkoxycarbonyl moiety to a positive migration terminus is an intriguing transformation since the migrating carbon should also have a partial positive charge due to the normal polarization of the carbonyl group.[8] In general, two transition states for carbonyl migration have been invoked that differ primarily in the degree of concertedness with respect to migration and departure of the leaving group at the migration terminus. A classical experiment used to distinguish between the intermediacy of a long-lived carbocation such as **1** or a concerted mechanism (i.e., **2**[9]) involves the use of an optically active substrate. Glycidic ester **3** was chosen for



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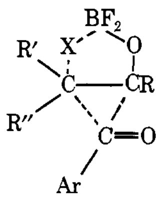

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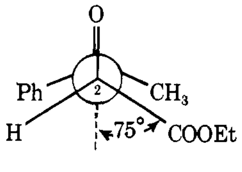


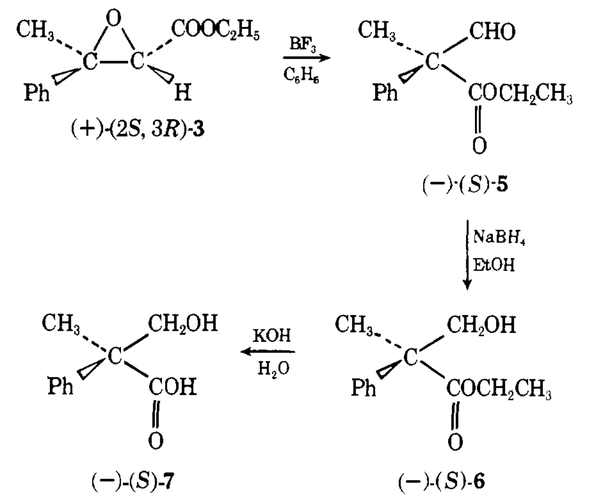
3

X = F, O(C$_2$H$_5$)$_2$

this experiment since it has no β-hydrogens and is not subject to decarboxylation or enolization following the migration step. This substrate will also provide a rigorous test for a concerted process because the dihedral angle between the σ bond of the migrating carbethoxy group and the developing p orbital at C$_3$ is ~75° (**3**). Since the migrating moiety cannot readily assume a conformation anti to the incipient empty p orbital, considerable C$_2$–C$_3$ bond rotation must occur late along the reaction coordinate of a concerted reaction. We now report that ethyl (+)-(2*S*,3*R*, E)-3-methyl-3-phenylglycidate (**3**) rearranges by the action of boron trifluoride to afford ethyl (−)-(*S*)-2-formyl-2-methylphenylacetate (**5**) with complete inversion of configuration at the migration terminus (Scheme I).

Optically active sodium (*E*)-3-methyl-3-phenylglycidate (**4**) was obtained by classical resolution with brucine;[10] $[\alpha]^{25}\mathrm{D}$ 85.7° (*c* 2.4, H$_2$O). Treatment of **4** with silver nitrate and ethyl iodide gave ethyl (+)-(2*S*, 3*R*, *E*)-3-methyl-3-phenylglycidate (**3**); $[\alpha]^{25}\mathrm{D}$ 113.8° (*c* 1.7, CHCl$_3$). The enantiomeric purity of **4** was established as essentially 100% by using a chiral europium shift reagent.[10,14] The NMR experiments established that a discernible amount of the other enantiomer, (−)-**3**, was not in evidence. Addition of a known amount of racemic **3** to the above sample showed that the two enantiomers exhibited a frequency difference in the resonance for the methine protons and the oxirane methyl groups of 10.5 and 21.0 Hz, respectively. Integration of these NMR signals established the enantiomeric ratio of **3** to be >98:2. Similar experiments with the methyl ester of optically pure **4** were in complete agreement.

Scheme I



The rearrangement of (+)-**3** was carried out at 25° in a benzene solution saturated with boron trifluoride.[4] Purification of the product by column chromatography (silica gel) and preparative GLC afforded ethyl (−)-(*S*)-2-formyl-2-methylphenylacetate (**5**) (44.8%), $[\alpha]^{25}\mathrm{D}$ 109.2° (*c* 1.13, CHCl$_3$). The enantiomeric purity of **5** was established using the europium chiral shift reagent[10] and found to be identical (98:2) with that of the starting material ((+)-**3**) within experimental error. These data establish that carbethoxy migration occurs with *no detectable loss of optical purity*.

The absolute configuration of the rearrangement product (**5**) was established by reduction with sodium borohydride in absolute ethanol. Preparative GLC afforded (−)-(*S*)-**6** (73%), $[\alpha]^{25}\mathrm{D}$ −25.7° (*c*, 1.4 CHCl$_3$). Saponification of **6** gave (−)-(S)-α-methyltropic acid (**7**) (55%), $[\alpha]^{25}\mathrm{D}$ −26.3° (*c* 1.83, EtOH) (lit.[15] 27°, *c* 2, EtOH) of known absolute configuration.[16,17] The results establish that carbethoxy migration has occurred with *inversion of configuration* at the migration terminus.

In conclusion, we have shown that ethoxycarbonyl migration in (+)-**3** occurs with inversion of configuration. Our findings are significant in that they preclude the intermediacy of a long-lived carbocation and provide evidence that these reactions proceed with a high degree of concertedness.

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the resulting two diols to (−)-(*S*)-2-phenyl-2-butanol and (−)-(*R*)-2-phenylpropionic acid (hydratropic acid).[13] Rearrangement of **3** utilized the procedure of Kagan.[4] The optical purity of **3** and **5** was established by using the europium chemical shift reagent "Eu-Opt" (Ventron, Beverly, Mass.) in CCl_4 solvent.

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Coupling Constants between Directly Bonded Silicon Atoms

Sir:

The recent widespread availability of pulsed Fourier transform (FT) NMR has resulted in a substantial surge of activity related to direct observation of the silicon-29 nucleus at its 4.7% natural abundance. To date, however, no reports of coupling between directly bonded silicon nuclei have appeared in the literature; the only silicon-silicon coupling constant which has been reported[1] is J_{SiOSi} for $(Me_3SiO)_4Si$. We wish to report the first examples of directly bonded Si-Si coupling constants for some linear and neopentyl disilanes and polysilanes.[2]

Parameters related to ^{29}Si NMR for the compounds selected for this study are presented in Table I. The spectra of the central silicons in $(Me_3Si)_4Si$ (**1**) and $(Cl_3Si)_4Si$ (**10**) are shown in Figures 1 and 2. All spectra except that for **10** were obtained with complete proton decoupling (where appropriate) on Varian XL-100-15 NMR spectrometers operating in the FT mode at 19.9 MHz for ^{29}Si. The spectrum of **10** was obtained on a JEOL-FT-1A (^{29}Si at 19.8 MHz) instrument. A small amount of $Cr(acac)_3$ was added to each sample to shorten the long silicon spin-lattice relaxation times and suppress the negative NOE arising from proton decoupling.[4] The Si-C coupling constants of **9** were confirmed in the ^{13}C spectrum obtained on a Varian CFT-20 spectrometer operating in the FT mode at 20 MHz for ^{13}C. First order (or nearly so) spectra were obtained for

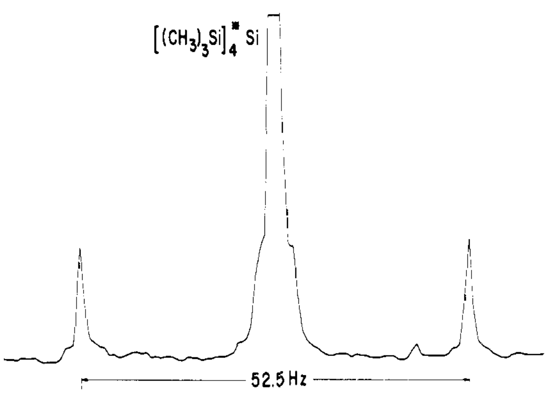

Figure 1. Silicon-29 NMR spectrum of the central silicon in $[(CH_3)_3Si]_4Si$.

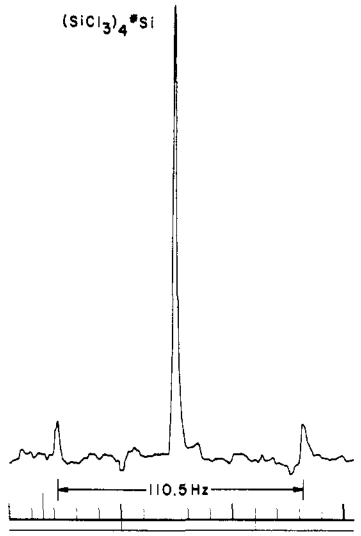

Figure 2. Silicon-29 NMR spectrum of the central silicon in $(SiCl_3)_4\underset{*}{Si}$.

Table I. Silicon-29 Chemical Shifts and Coupling Constants[a]

Compound	A, δ	B, δ	Solvent	$\lvert ^1J_{SiSi}\rvert$	$^1J_{Si^AC}$	$^1J_{Si^BC}$
$(Me_3Si^A)_4Si^B$ (**1**)	−9.8	−135.5	$CDCl_3$	52.5	44.7	—
$(Me_3Si^A)_2Si^BMe_2$ (**2**)	−16.1 (−15.93)[b]	−48.7 (−48.45)[b]	$CDCl_3$	73.2	43.8	37.0
$Me_3Si^ASi^BMe_2H$ (**3**)	−18.9	−39.1	Acetone-d_6	84.6	44.6	43.8
$Me_3Si^ASi^BMe_2Ph$ (**4**)	−19.3	−21.7	Acetone-d_6	86.1	44.1	44.8
$Me_3Si^ASi^BPh_3$ (**5**)	−18.4	−20.2	$CDCl_3$	86.5	*[c]	*[c]
$Me_3Si^ASi^BMe_2Cl$ (**6**)	−18.2	+22.8	$CDCl_3$	94.0	46.2	45.9
$(Me_3Si^ASi^BMe_2)_2NH$ (**7**)	−22.0	−5.4	C_6D_6	96.0	42[c]	46.6
$Me_3Si^ASi^BMe_2F$ (**8**)	−22.5	+34.0	C_6D_6	98.7 ($^1J_{SiF}$ = 306.8, $^2J_{SiF}$ = 26.7)	*[c]	47.9
$(Me_3Si^ASi^BMe_2)_2O$ (**9**)	−23.1	+5.2	$CDCl_3$	103.4	43.8	48.0
$(Cl_3Si^A)_4Si^B$ (**10**)	+3.5	−80.0	$CDCl_3$	110.5	—	—
$(MeO)_3Si^ASi^BPh_3$ (**11**)	−45.9	−29.2	$CDCl_3$	160.0	—	*[c]
$(Cl_3Si^A)_2Si^BCl_2$ (**12**)	−3.5	−7.2	C_6D_6	186	—	—

[a] All chemical shifts are given in ppm relative to internal tetramethylsilane (Me_4Si) except for **10** and **12** which are relative to external Me_4Si. Negative values correspond to upfield shifts. Coupling constants are given in Hz. Silicon-silicon couplings from all ^{29}Si spectra except those of **4**, **5**, and **12** were determined from satellites of both Si^A and Si^B lines to an estimated accuracy of ±0.5 Hz. Spectra of **1** and **10** were first order; all the rest were assigned as AB spin systems. Only the two central lines of the quartet were observed for $^1J_{SiSi}$ of **4**, **5**, and **12** (estimated accuracy for **4** and **5** is 0.5 Hz; for **12**, ±2 Hz). [b] Literature values from ref 3. [c] Assignments for $^1J_{SiC}$ not clear.